



EUROPEAN PATENT APPLICATION

Application number: **91300871.0**

Int. Cl.⁵: **C07C 271/22, C08F 18/00,
C11D 3/37**

Date of filing: **04.02.91**

Priority: **06.02.90 US 475660**
06.02.90 US 475666

Date of publication of application:
14.08.91 Bulletin 91/33

Designated Contracting States:
CH DE ES FR GB IT LI NL SE

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Vinyl carbamate compounds and detergent compositions containing them.

Novel vinyl carbamates, prepared from vinyl chloroformate and amino acids, and homo- and co-polymers containing from 5 to 100% of units of these novel vinyl carbamates, are disclosed. These polymers act as sequestering agents and are useful as detergency builders. Detergent compositions incorporating the polymers can be prepared without the use of phosphorus-containing detergent builders.

VINYL CARBAMATE COMPOUNDS AND THEIR USE IN DETERGENT COMPOSITIONS

TECHNICAL FIELD

The present invention relates to novel vinyl carbamates and polymers including these vinyl carbamates. These novel compounds are effective chelating agents and useful in detergent compositions. These
 5 polymers may also be used as antiredeposition agents, dispersants, scale inhibitors, bleach stabilising agents and in a variety of other applications which require hardness sequestration or crystal modification.

BACKGROUND AND PRIOR ART

10 Builders are desirable ingredients in powdered detergent formulations, which optimise the effectiveness of surfactants by sequestering calcium, magnesium and other "hardness" ions present in the wash water that adversely affect detergency.

The manner in which detergent builders improve the cleaning powers of detergent compositions is related to a combination of factors such as emulsification of soil particles, solubilisation of water-insoluble
 15 materials, promotion of oil suspension in the wash water so as to retard soil redeposition, sequestration of metallic ions, and the like.

Phosphates, such as tripolyphosphates and pyrophosphates, are widely used as builders due to their excellent ability to sequester "hardness" ions. However, the effect of phosphates upon the eutrophication of lakes and streams has been questioned and their use in detergent compositions has been subject to
 20 government scrutiny and regulation. Alternatives for phosphates are widely used by detergent formulators as builders in detergent formulations. Compositions and materials change frequently as formulators attempt to improve cleaning performance while offering greater convenience in handling at lower material cost. The industry has made substantial efforts to find suitable substitutes for phosphates, however, all have one or more drawbacks that offset their value in the formulations.

25 FR 2 612 521 (Bernard Brosse) discloses selected chelating polymers similar to those of the invention.

US 3 711 458 and US 3 835 109 (Olofson) disclose processes for peptide synthesis employing a vinyloxy carbonyl group as a protecting group.

US 3 923 742 (Haschke) discloses a process for producing a polycarboxylate phosphate substitute said to be readily biodegradable.

30 US 4 559 159 (Denzinger et al) discloses water-soluble copolymers for use with detergents.

While polymeric carboxylates have been found to be suitable builders, few have been found to be biodegradable, indeed, few synthetic polymers have been found to be biodegradable. One method of improving the biodegradability of synthetic polymers has been to incorporate hydrolysable linkages within the main polymer backbone. This approach, however, usually does not produce high molecular weight
 35 polymers. A second method of improving biodegradability is a method of this invention, namely to couple relatively small biodegradable carboxylates to a polymer backbone which will, through hydrolysable linkages, break down to form polyvinyl alcohol (PVA) or a PVA-like copolymer. Upon hydrolysis, the components are then expected to be biodegradable.

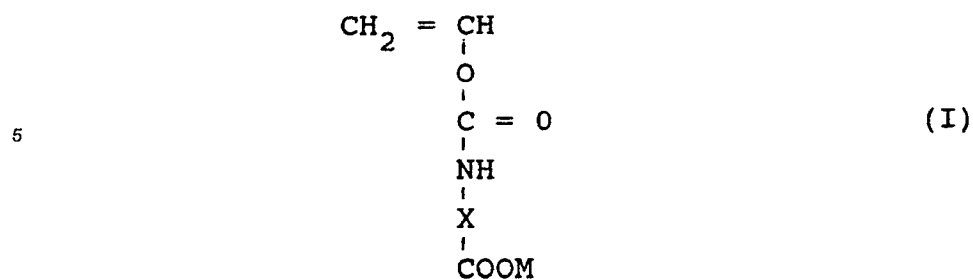
The polymeric builders herein described contain carbamate linkages with environmentally acceptable
 40 amino acids. While not wishing to be bound by theory, it is theorised that the carbamate linkages will break down in the environment to polyvinyl alcohol plus the corresponding amino acid, all of which are reported to be relatively environmentally acceptable. Further, the electrostatic and site specific charge interactions of the compounds of this invention contribute to the builder efficiency.

The polymers of the invention are effective "hardness" ion sequestering agents which may be
 45 employed in detergent compositions as a replacement, in whole or in part, for phosphate builders.

DEFINITION OF THE INVENTION

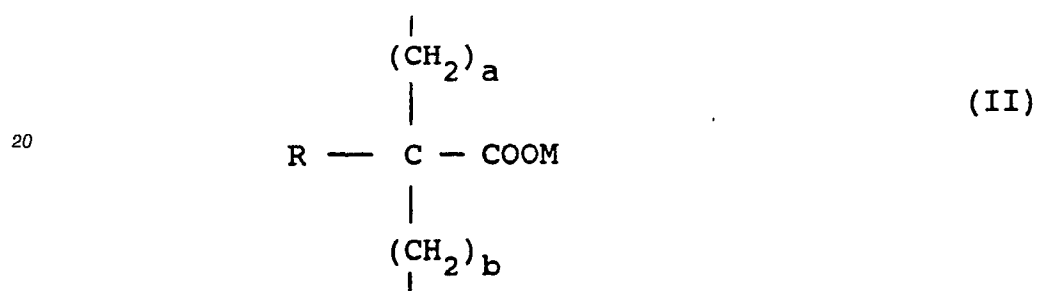
The invention broadly includes novel monomeric compounds; novel homo- and co-polymers of those
 50 monomers; and detergent compositions containing the polymers.

The novel monomeric compounds of the invention are vinyl carbamates of the general Formula I:

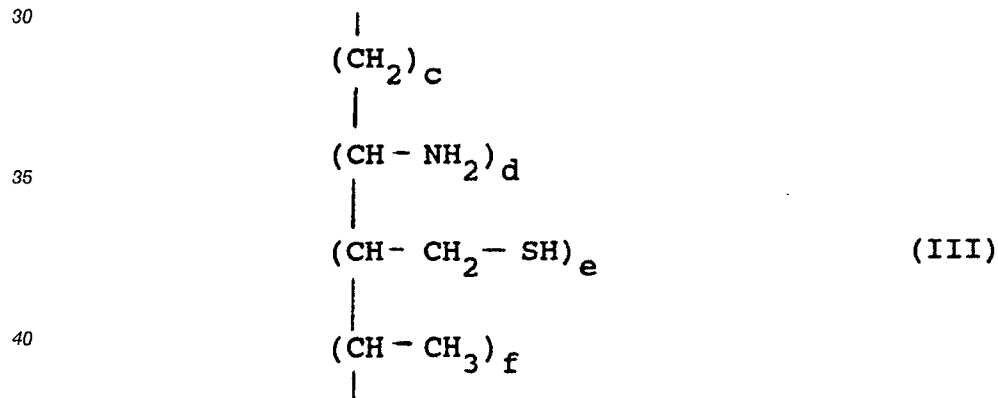


wherein M is a C₁₋₄ alkyl, hydrogen or a cation which forms a substantially water-soluble salt with said compound at ambient temperatures, and X is either

i) a group of the formula II:



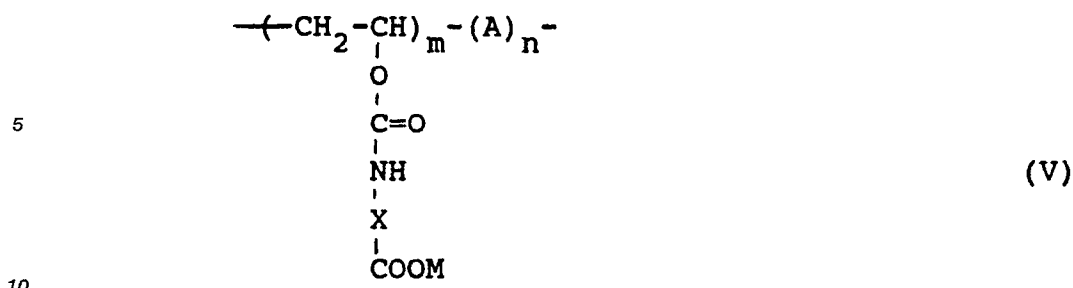
wherein a is 0 or a positive integer, and b is 0 or a positive integer, or
ii) a group of the formula III:



wherein c is 0 or an integer of 1 to 4; d is 0 or 1, e is 0 or 1 and f is 0 or 1 but d+e+f is 0 or 1; provided that when d is 1, c is 3 or 4; when e is 1, c is 0; and when f is 1, c is 0.

When X has the formula II, a and b are preferably independently 0, 1 or 2.

Another aspect of the invention provides polymers comprising units of the novel vinyl carbamates of Formula I. The polymers have the general formula V:

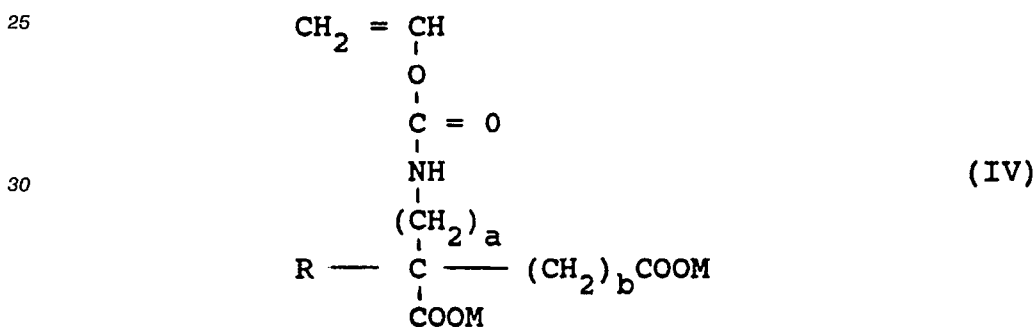


wherein m represents the number of repeating units of the vinyl carbamate monomer and is at least 1; n represents the number of repeating units of the vinyl carbamate comonomer and is 0 or an integer of at least 1; M is hydrogen, C₁₋₄ alkyl or a cation which forms a substantially water-soluble salt with said polymeric compound at ambient temperatures; X is as defined above, and A is a unit comprised of at least one copolymerisable comonomer.

DETAILED DESCRIPTION OF THE INVENTION

The vinyl carbonate monomers

A preferred class of vinyl carbonate monomers within the formula I is represented by the formula IV:



wherein a and b are independently 0 or a positive integer, preferably 0, 1 or 2; R is hydrogen methyl, ethyl or long-chain alkyl, alkenyl or aryl and M is C₁₋₄ alkyl, hydrogen, or a cation which forms a substantially water-soluble salt with said compound at ambient temperatures.

Preferably, when a is 0, b is 0 or 2 and R is hydrogen; when a is 0 and b is 1, R is hydrogen or methyl; and when a is 1 and b is 0, R is hydrogen.

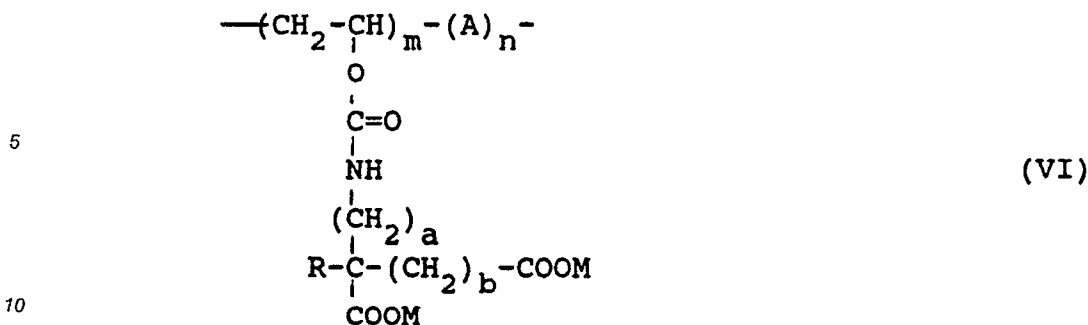
M is preferably hydrogen, ammonium or an alkali metal.

It is also preferred that the novel vinyl carbamates as defined by formulae I and IV have substantial water solubility.

The vinyl carbonate polymers

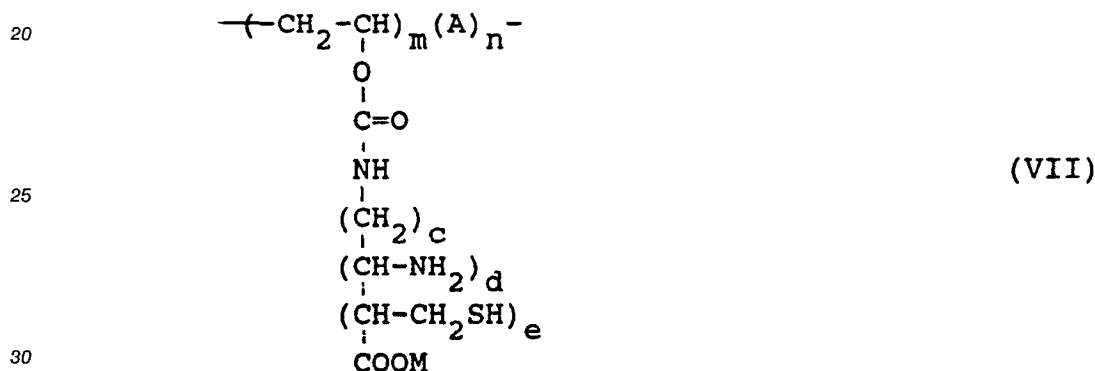
The invention also provides both homopolymers and copolymers of the vinyl carbamate monomers defined above. The polymers may be prepared from the vinyl carbamates by either free radical homopolymerisation or by copolymerisation with one or more other ethylenically unsaturated polymerisable comonomers. Thus, polymers containing two, three or even more comonomers may be employed.

A first preferred class of polymers within the formula V is represented by the formula VI:



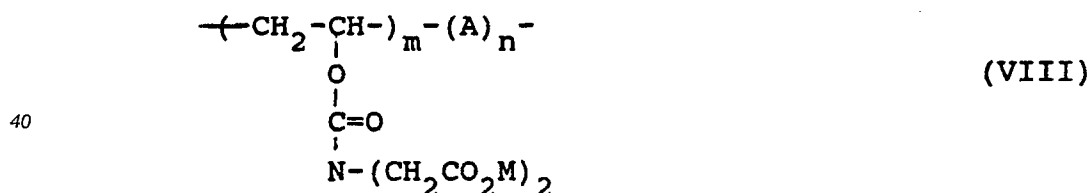
wherein m, n, A, a, b and M have the meanings given previously. Preferably a and b are independently 0 or an integer of 1 or 2. R is preferably hydrogen or methyl and M is preferably hydrogen, ammonium or an alkali-metal. More preferably, when a is 0, b is 0 or 2, R is hydrogen; when a is 0, b is 1, R is hydrogen or methyl; and when a is 1, b is 0, R is hydrogen.

A second preferred class of polymers within the formula V is represented by the formula VII:



wherein m, n, A, c, d and e have the meanings given previously.

A third preferred class of polymers of the invention is represented by general formula VIII:



wherein M, A, m and n are as defined above.

The comonomer

The comonomer providing the units A is an ethylenically unsaturated compound, preferably one copolymerisable with vinyl acetate and/or ethylene.

Suitable comonomers (A) include ethylenically unsaturated carboxylic acids and their salts, esters and derivatives, such as acrylic acid, methacrylate, methyl methacrylate, crotonic acid, N-methylacrylyl-D-glucosamine, vinyl benzoic acid, vinylacetic acid, methyl acrylate, itaconic acid, acylamide and methyl acrylamide; ethylenically unsaturated dicarboxylic acids and their salts, esters, anhydrides and derivatives such as fumaric acid, maleic acid and maleic anhydride; ethylenically unsaturated alcohols such as allyl alcohol; ethylenically unsaturated amines such as allyl amine; ethylenically unsaturated pyrrols such as N-vinylpyrrolidinone; vinyl ethers such as methyl vinyl ether; alkyl acrylates; alkenyl carboxyalkyl ethers; vinyl esters of carboxylic acids; alkenyl aryls such as vinyl benzene, polymerisable derivatives of 4-hydroxy-2,6-

pyridine dicarboxylic acid; 2,6-pyridine dicarboxylic acid and vinyl pyridine; alkenyl aldehydes such as acrolein; acrylonitrile; methacrylonitrile; olefins and furans.

Suitable vinyl esters of alkanolic acids which may be employed are those having from 1 to 13 carbon atoms and include, for example, vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl 2-ethyl-hexanoate, vinyl isooctanoate, vinyl nonoate, vinyl decanoate, vinyl pivalate, etc.

Those skilled in the art will recognise that the preferred selection of comonomers will be those comonomers best suited to the polymers' intended use. Thus, for detergent use, comonomers with known effectiveness as "hardness" ion sequestrants or as detergent builders are selected. Other factors, such as cost and detergent formulation compatibility will also guide comonomer selection.

Optionally, polyunsaturated polymerisable comonomers may also be present in small amounts, ie up to 5% by weight. Such comonomers include those polyethylenically-unsaturated monomers such as lower alkenyl lower alkenoates, for example, vinyl crotonate, allyl acrylate, allyl methacrylate; di-lower alkenyl alkanedioates, for example, diallyl maleate, divinyl adipate, diallyl adipate; di-lower alkenyl benzenedicarboxylates, for example diallyl phthalate; lower alkanediol di-lower alkenoates, for example ethylene glycol diacrylate, ethylene glycol dimethacrylate, butanediol dimethacrylate; lower alkylene bis-acrylamides and lower alkylene bis-methacrylamides, for example, methylene bis-acrylamide; triallyl cyanurate, etc.

Batch, semi-batch or slow addition methods may be used to prepare the homopolymers or copolymers of the invention. In accordance with either the batch or semi-batch procedures, the initiator(s), any optional comonomers and the novel carbamate monomer are polymerised in aqueous medium under pressures not exceeding 100 atmospheres in the presence of a catalyst, the aqueous system being maintained by a suitable buffering agent at a pH of 2 to 10, the catalyst being added incrementally or continuously. Suitable as polymerisation catalysts are the water-soluble free-radical formers generally used in polymerisation, such as azobisisobutyronitrile (AIBN), hydrogen peroxide, sodium persulphate, potassium persulphate and ammonium persulphate, as well as tert-butyl hydroperoxide, in amounts of 0.01 to 15% by weight, preferably 0.01 to 1% by weight based on the total amount of monomer(s). The free-radical formers can be charged in the aqueous solution or added during the polymerisation in doses.

The polymerisation may be carried out at a pH of between 2 and 10, preferably between 3 and 5. In order to maintain the pH range, customary buffer systems may be used. For example, alkali-metal acetates, alkali-metal carbonates, alkali-metal phosphates and the like. Polymerisation regulators, such as mercaptans, aldehydes, chloroform, methylene chloride, and trichloroethylene can also be added in some cases.

The polymers according to the invention preferably contain at least 5% of units derived from the vinyl carbamate monomer of the formula I, i.e. units of the formula IV in which n is zero. Since homopolymers may be used, the actual vinyl carbamate unit content is therefore preferably from 5 to 100%. The polymers may be copolymers, terpolymers or other higher combinations of polymerisable comonomers. In this case, the polymer contains not only vinyl carbamate units but also other repeating units derived from ethylenically unsaturated comonomers, in order to vary the properties of the polymer and particularly its solubility.

The polymers according to the present invention suitably have a molecular weight of from 1000 to 750000, and preferably of 5000 to 400000.

The molecular weight of the polymers can be controlled by the usual methods, for example, by varying the concentration of monomer(s), initiator(s) and chain-transfer agent(s).

For detergent and sequestrant use, the polymers must be sufficiently water-soluble to function as a builder to sequester hardness ions such as calcium, magnesium and the like.

It will be found that the biodegradability of selected polymers is enhanced by the incorporation into these polymers of the novel carbamate monomers of the formula I. The polymers which are expected to benefit from such introduction are generally polymers formed from ethylenically unsaturated monomers copolymerisable with vinyl acetate and/or ethylene. Examples of such monomers include ethylenically unsaturated carboxylic acids and their salts, esters, and derivatives such as acrylic acid, methacrylate, methyl methacrylate, crotonic acid, N-methylacrylyl-D-glucosamine, vinyl benzoic acid, vinylacetic acid, itaconic acid, acrylamide, and methyl acrylamide; ethylenically unsaturated dicarboxylic acids and their salts, esters, anhydrides and derivatives such as fumaric acid, maleic acid and maleic anhydride; ethylenically unsaturated alcohols such as allyl alcohol; ethylenically unsaturated amines such as allyl amine; ethylenically unsaturated pyrrols such as N-vinylpyrrolidinone; vinyl ethers such as methyl vinyl ether; alkyl acrylates; alkenyl carboxyalkyl ethers; vinyl esters of carboxylic acids; alkenyl aryls such as vinyl benzene and vinyl pyridine; alkenyl aldehydes such as acrolein; acrylonitrile; methacrylonitrile; olefins and furans.

The detergent compositions

Polymers of the present invention, when in substantially water-soluble salt form, can be used as sequestering agents in a wide variety of detergent or laundry additive compositions.

Detergent compositions are generally a blend of a surfactant(s), builder(s) and, optionally, ion exchanger(s), filler(s), alkali(s), anticorrosion material(s), antiredeposition material(s), bleach(es), enzyme(s), optical brightener(s), fragrance(s) and other components selected for particular applications.

Detergent compositions incorporating the polymeric salt of the invention contain as essential components from 0.5% to 98% of a surfactant and from 2% to 99.5% of the polymeric compounds as a detergency builder, suitably in the sodium or ammonium salt form.

Preferably the detergent composition contains, in percent by weight of the composition: (a) 10-60% builder consisting of or including the polymeric compounds of the invention; (b) 2-25% surfactant; (c) optionally, 30% of other ingredients and a sufficient amount of water to either insure fluidity in the case of a liquid or to enhance processibility in the case of a solid granular or powdered detergent.

Surfactants that are useful in the present invention are the anionic (soap and non-soap), nonionic, zwitterionic and ampholytic compounds. The chemical nature of these detergent compounds is not an essential feature of the present invention. Moreover, such detergent compounds are well known to those skilled in the detergent art and the patent and printed literature are replete with disclosures of such compounds. Typical of such literature are "Surface Active Agents" by Schwartz and Perry and "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, the disclosures of which are incorporated by reference herein.

The polymeric builder can be used either as the sole builder or, where desired, can be used in conjunction with other well-known builders, examples of which include water-soluble salts of phosphates, pyrophosphates, orthophosphates, polyphosphates, phosphonates, carbonates, carboxylates, polycarboxylates, succinates and the like.

In addition to the surfactant and builder, there may be optionally present additional ingredients which enhance the performance of the detergent composition. Typical examples of these include the well-known soil suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers, optical brighteners, enzymes, suds boosters, suds depressants, germicides, anti-tarnishing agents, cationic detergents, softeners, bleaches, buffers and the like. Other ingredients which may be optionally employed are such components as colouring dyes, suds stabilisers (eg dibutyl phthalate), fluorescent dyes, enzymes, perfumes, antiredeposition agents (eg carboxymethylcellulose), soil shield agents (eg hydropropyl methyl cellulose), bleaches, neutralised copolymers of ethylene and maleic anhydrides (eg EMA resins manufactured by the Monsanto Company), co-surfactants and the like. Co-surfactants may be selected from the group consisting of anionic, cationic and zwitterionic surfactants and mixtures thereof. The bleaches may be chlorine or oxygen release types. The amounts of these additional ingredients or adjuvants may range from 0 to 30% by weight of the composition. Some of the adjuvants may be incorporated during the slurry preparation and others, because of stability considerations, may be post added to a spray-dried product as well known to those skilled in the art.

The detergent compositions of the present invention may be in any of the usual physical forms for such compositions, such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes and the like.

The detergent compositions are prepared and utilised in the conventional manner. The wash solutions thereof desirably have a pH of 7 to 12, preferably 9 to 11 and contain typically 0.001 to 0.5% and preferably 0.009% to 0.3% by weight of the detergent composition and a corresponding amount of the polymeric compounds of this invention, preferably, for example, 0.005% to 0.3% by weight.

In addition to their utility as builders in detergent and laundry additive compositions, the polymeric salts of the invention can also be utilised in other contexts wherein water hardness sequestration is required. Other uses are provided in water softening compositions, devices and methods, bleach stabilisation compositions, and boiler descaling compositions and methods.

Synthesis of vinyl carbamate monomers

Vinyl carbamates may be prepared via the reaction of vinyl chloroformate and the corresponding amino acid which may be, for example, aspartic acid, N-methyl aspartic acid, aminoadipic acid, glutamic acid, 2-methyl glutamic acid, aminomalonic acid, glycine, alanine, aminobutyric acid, cysteine, ornithine or iminodiacetic acid to yield the corresponding N-VOC (N-vinyloxy carbonyl) amino acid defined in Formulae (1) and (2). The HCl produced during the reaction may be neutralised by using at least one additional equivalent of amino acid or other base. Acetonitrile, dioxane/water, or other solvent systems may be used in the preparation of these novel vinyl carbamates. Reaction temperatures and times will, of course, vary for different amino acids.

Preparation of vinyl carbamate polymers

Vinyl carbamate copolymers may be prepared via the free radical polymerisation of a vinyl carbamate with an ethylenically unsaturated polymerisable comonomer.

- 5 Polymerisation of these novel vinyl carbamates is preferably accomplished in aqueous solution at temperatures of 5-85 °C, but preferably at temperatures of 25-65 °C with concentrations varying from 1-80%. Polymerisations may be initiated with potassium persulphate but other initiators such as peroxides may also be used.

The following non-limiting Examples illustrate the invention.

- 10 All parts, percentages, and proportions herein and in the appended claims are by weight unless otherwise specified.

EXAMPLES15 EXAMPLES 1-4: MONOMER SYNTHESISExample 1: Preparation of N-Vinyloxy Carbonyl (N-VOC) Aspartic Acid

- Aspartic acid (20.0g, 0.150 mol) was added to a flask containing 180 ml of acetonitrile. Vinyl
20 chloroformate (8.0g, 0.075 mol) was added to the mixture and the mixture was agitated. The mixture was refluxed with continued agitation for 2 hours and cooled to room temperature. The reaction mixture was then filtered. Solvent was removed from the filtrate in vacuo to yield N-VOC aspartic acid. The product was characterised by NMR (¹H and ¹³C) and mass spectrometry. ¹H NMR (200 MHz, acetone-d₆) δ2.96 (2H, dd, -CH₂CO₂H), 4.44, 4.71, 7.20 (3H, m, CH₂ = CH-), 4.66 (1H, m, -CH(CO₂H)).

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Example 2: Preparation of N-VOC Glutamic Acid

- Glutamic acid (20.0g, 0.121 mol) was added to a flask containing 180 ml of acetonitrile. Vinyl
30 chloroformate (6.4g, 0.060 mol) was added to the mixture and the mixture was agitated. The mixture was refluxed for 2 hours with continued agitation and cooled to room temperature. The reaction mixture was then filtered. Solvent was removed from the filtrate in vacuo to yield N-VOC glutamic acid. The product was characterised by NMR (¹H and ¹³C) and mass spectrometry. ¹H NMR (200 MHz, acetone-d₆) δ2.08 (2H, m, -CH₂-), 2.39 (2H, t, -CH₂CO₂H), 4.20 (1H, m, -CH(CO₂H)-), 4.29, 4.57, 7.04 (3H, m, CH₂ = CH-).

35 Example 3: Preparation of N-Vinyloxy Carbonyl (N-VOC) Glycine

- Glycine (17.0g, 0.226 mol) was added to a flask containing 100 ml of acetonitrile. Vinyl chloroformate
40 (12.5g, 0.117 mol) was added to the mixture and the mixture was agitated. The mixture was stirred at room temperature for 72 hours and filtered. Solvent was removed from the filtrate in vacuo to yield N-VOC glycine. The product was characterised by NMR (¹H and ¹³C) and mass spectrometry.

Example 4: Preparation of N-VOC Alanine

- Alanine (20.0g 0.224 mol) is added to a flask containing 180 ml of acetonitrile. Vinyl chloroformate
45 (12.0g, 0.112 mol) is added to the mixture and the mixture is agitated. The mixture is refluxed for 2 hours with continued agitation and cooled to room temperature. The reaction mixture is then filtered. Solvent is removed from the filtrate in vacuo to yield N-VOC Alanine. The product is characterised by NMR (¹H and ¹³C) and mass spectrometry.

50 EXAMPLES 5-8: POLYMER SYNTHESISA General Method for Preparing Poly(vinyl carbamates)

- An aqueous solution of monomers (30-50% w/w) is sparged with a steady stream of nitrogen for 1 hour.
55 Polymerisation is initiated with potassium persulphate (1% of the total weight of monomers). The solution is stirred at ambient temperatures and then heated to a range of about 35-70 °C until an increase in viscosity is noted. The polymer is isolated by precipitating from a non-solvent.

Example 5: Preparation of Acrylic Acid/N-VOC Aspartic Acid Copolymer

Acrylic Acid (2.9g, 0.040 mol) and N-VOC aspartic acid (2.0g, 0.010 mol, Example 1) were dissolved in 25 ml of water. The solution was then sparged with a steady stream of nitrogen for 1 hour. Potassium persulphate (0.05g, 1.8×10^{-4} mol) was then dissolved in the solution. The solution was stirred at 70 °C for 16 hours to allow polymerisation. The polymer was then isolated by precipitation in acetonitrile. The precipitated polymer in turn was analysed by GPC and NMR (^1H and ^{13}C). Nitrogen analysis of the polymer showed 11 molar % incorporation of the carbamate monomer. GPC analysis showed a molecular weight (Mw) of >750,000. Calcium binding studies of this polymer showed an upper log K_{ca} value of 5.3 with unoccupied binding sites and a log K_{ca} value of 4.5 with 50% of the binding sites occupied.

Example 6: Preparation of Maleic Acid/N-VOC Aspartic Acid Copolymer

Maleic Acid (3.0g, 0.026 mol) and N-VOC aspartic acid (5.2g, 0.026 mol, Example 1) were dissolved in 25 ml of water. The solution was then sparged with a steady stream of nitrogen for 1 hour. Potassium persulphate (0.08g, 3.0×10^{-4} mol) was then dissolved in the solution. The solution was stirred at 70 °C for 16 hours to allow polymerisation. The polymer was then isolated by precipitation in acetone. The precipitated polymer in turn was analysed by GPC and NMR (^1H and ^{13}C). Nitrogen analysis of the polymer showed a 50 molar % incorporation of the carbamate monomer. GPC analysis showed a molecular weight (Mw) of 100,000. Calcium binding studies of this polymer showed an upper log K_{ca} value of 6.5 with unoccupied binding sites and a log K_{ca} value of 4.8 with 50% of the binding sites occupied.

Example 7: Preparation of Maleic Acid/N-VOC Glycine Copolymer

Maleic acid (9.6g, 0.083 mol) and N-VOC glycine (12.0g, 0.083 mol, Example 3) were dissolved in 54 ml of water. The solution was then sparged with a steady stream of nitrogen for 1 hour. Potassium persulphate (0.2g, 7.4×10^{-4} mol) was then dissolved in the solution. The solution was stirred at 65 °C for 16 hours to allow polymerisation. The polymer was then isolated by precipitation in acetone. The precipitated polymer in turn was analysed by GPC and NMR (^1H and ^{13}C). Nitrogen analysis of the polymer showed a 50 molar % incorporation of each comonomer. GPC analysis showed a molecular weight (Mw) of 360,000. Calcium binding studies of this polymer showed an upper log K_{ca} value of 6.1 with unoccupied binding sites and a log K_{ca} value of 2.4 with 50% of the binding sites occupied.

Example 8: Preparation of Maleic Acid/N-VOC Alanine Copolymer

Maleic acid (10.0g, 0.086 mol) and N-VOC alanine (13.7g, 0.086 mol) are dissolved in 60 ml of water. The solution is then sparged with a steady stream of nitrogen for 1 hour. Potassium persulphate (0.2g, 7.4×10^{-4} mol) is then dissolved in the solution. The solution is stirred at 65 °C for 16 hours to allow polymerisation. The polymer is then isolated by precipitation in acetone.

Determination of Calcium Binding

Calcium binding data was obtained at a pH of 10 by titrating 100 ml of 0.05g/l polymer solution at an ionic strength of 0.02-0.03 M (NaCl) with a 0.02 M CaCl_2 solution. A Radiometer (Trade Mark) calcium ion selective electrode was used to measure free Ca^{++} ion concentration of the solutions. Data was corrected for dilution during each titration.

TABLE 1

	5			6			A			B			C		
	Fraction Bound	Log K _{Ca}	Fraction Bound	Log K _{Ca}	Fraction Bound	Log K _{Ca}	Fraction Bound	Log K _{Ca}	Fraction Bound	Log K _{Ca}	Fraction Bound	Log K _{Ca}	Fraction Bound	Log K _{Ca}	Fraction Bound
1	0	5.30	0	6.90	0	6.10	0	4.80	0	4.80	0	6.80	0	6.80	0
2	0.18	5.30	0.36	5.74	0.29	5.13	0.14	4.32	0.35	4.32	0.35	5.43	0.35	5.43	0.35
3	0.25	4.97	0.41	5.21	0.33	4.91	0.23	4.11	0.43	4.11	0.43	5.10	0.43	5.10	0.43
4	0.33	4.84	0.46	5.02	0.36	4.75	0.27	3.95	0.52	3.95	0.52	4.85	0.52	4.85	0.52
5	0.40	4.72	0.50	4.77	0.40	4.56	0.32	3.82	0.60	3.82	0.60	4.58	0.60	4.58	0.60
6	0.47	4.59	0.55	4.62	0.43	4.45	0.36	3.69	0.66	3.69	0.66	4.34	0.66	4.34	0.66
7	0.54	4.48	0.59	4.48	0.46	4.33	0.39	3.56	0.71	3.56	0.71	4.16	0.71	4.16	0.71
8	0.61	4.39	0.63	4.33	0.49	4.23	0.41	3.45	0.74	3.45	0.74	3.98	0.74	3.98	0.74
9	0.67	4.29	0.67	4.23	0.52	4.16	0.44	3.32	0.75	3.32	0.75	3.80	0.75	3.80	0.75
10	0.73	4.24	0.71	4.16	0.54	4.08	0.46	3.24	0.76	3.24	0.76	3.68	0.76	3.68	0.76
11	0.82	4.21	0.78	4.14	0.59	3.91	0.47	3.10		3.10					

5 N-VOC aspartic acid/acrylic acid copolymer

6 N-VOC aspartic acid/maleic acid copolymer

A Builder U

B Polyacrylate

C Sokolan CP7

* values obtained by extrapolation

TABLE 2

		<u>Z</u>		<u>A</u>		<u>B</u>	
		<u>Fraction</u>	<u>Log</u>	<u>Fraction</u>	<u>Log</u>	<u>Fraction</u>	<u>Log</u>
		<u>Bound</u>	<u>K_{ca}</u>	<u>Bound</u>	<u>K_{ca}</u>	<u>Bound</u>	<u>K_{ca}</u>
5							
	1	0	6.10	0	6.10	0	4.80
10	2	0.25	5.47	0.29	5.13	0.14	4.32
	3	0.29	5.02	0.33	4.91	0.23	4.11
	4	0.33	4.81	0.36	4.75	0.27	3.95
15	5	0.37	4.66	0.40	4.56	0.32	3.82
	6	0.41	4.52	0.43	4.45	0.36	3.69
	7	0.45	4.39	0.46	4.33	0.39	3.56
20	8	0.48	4.26	0.49	4.23	0.41	3.45
	9	0.52	4.16	0.52	4.16	0.44	3.32
	10	0.55	4.04	0.54	4.08	0.46	3.24
25	11	0.58	3.95	0.59	3.91	0.47	3.10

7 N-VOC Glycine/Maleic acid copolymer

30 A Builder U

B Polyacrylate

35 * Values obtained by extrapolation

DESCRIPTION OF THE DRAWINGS

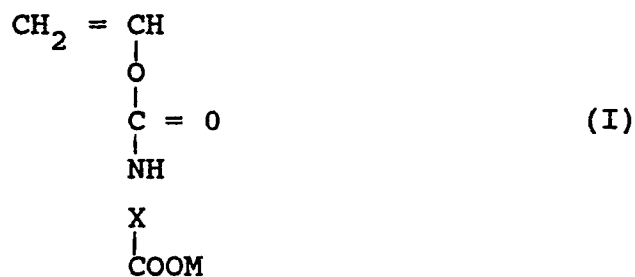
40 The Figures show log K_{ca} values versus the fraction of bound sites along the polymer. As polymeric sequestrants chelate hardness ions, the binding of the polymer decreases. This decrease in binding capability is illustrated in the Figures which clearly show the binding of the novel polymeric carbamate builders to be excellent.

45 Figure 1 reports calcium binding data for the polymers of Examples 5 and 6 and other previously reported polymeric builders. Builder U (polyglyoxylic acid) (A) was obtained from Monsanto and had a molecular weight (Mw) of 8,000. Polyacrylic acid (B) had a molecular weight (Mw) of 60,000 and Sokolan (Trade Mark) CP7 (C) (a 2:1 copolymer of acrylic acid/maleic acid obtained from BASF) had a molecular weight of 52,000. The actual values are reported in Table 1.

50 Figure 2 reports calcium binding data for the polymer of Example 7 and other previously reported builders - Builder U (A) and polyacrylic acid (B). The actual values are reported in Table 2.

Claims

55 1. A vinyl carbamate compound of the formula I:



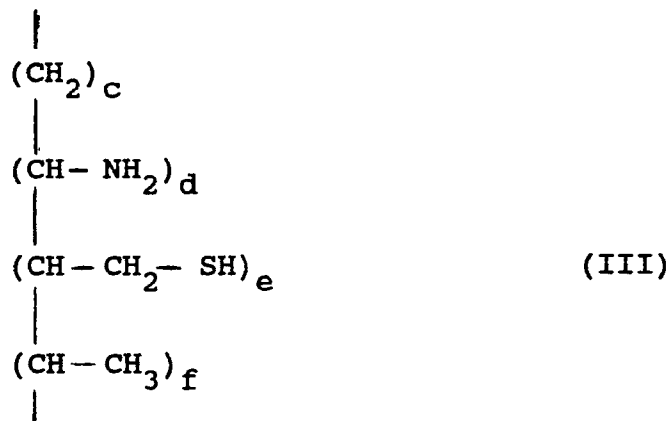
wherein M is a C₁₋₄ alkyl, hydrogen or a cation which forms a substantially water-soluble salt with said compound at ambient temperatures, and X is either

i) a group of the formula II:



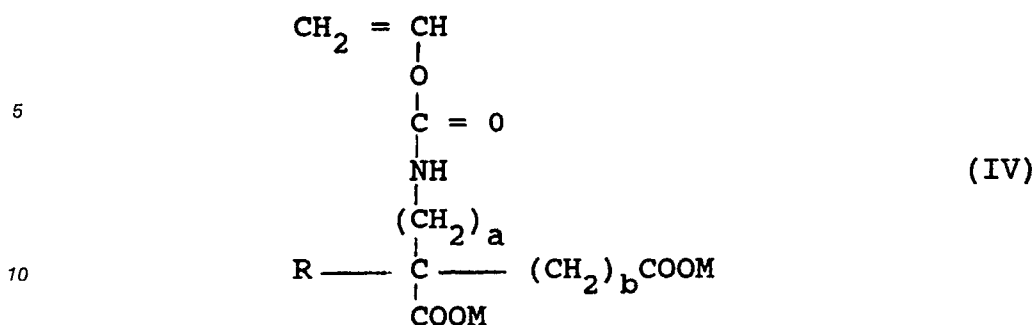
wherein a is 0 or a positive integer, and b is 0 or a positive integer, or

ii) a group of the formula III:



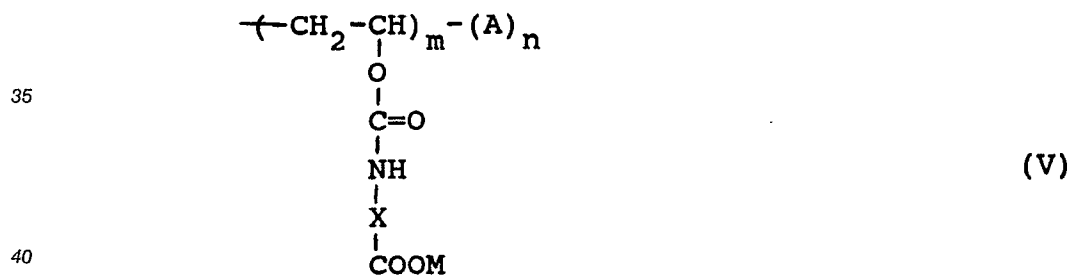
wherein c is 0 or an integer of 1 to 4; d is 0 or 1, e is 0 or 1 and f is 0 or 1 but d+e+f is 0 or 1; provided that when d is 1, c is 3 or 4; when e is 1, c is 0; and when f is 1, c is 0.

2. A vinyl carbamate compound as claimed in claim 1, characterised in that it has the formula IV:



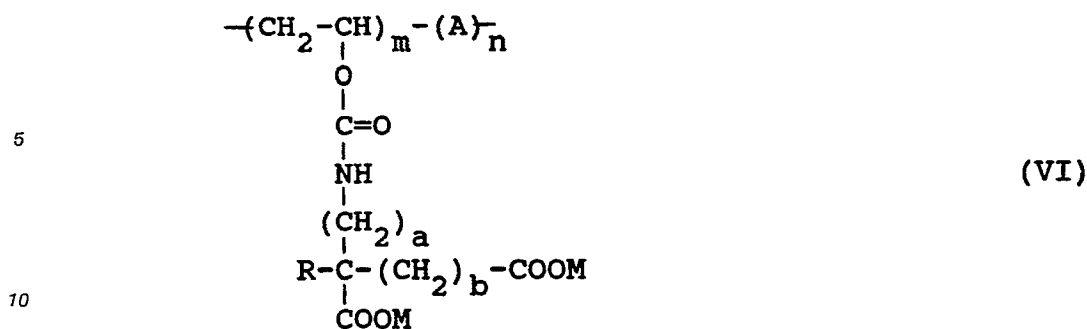
wherein a and b are independently 0 or a positive integer; R is hydrogen, methyl, ethyl or long-chain alkyl, alkenyl or aryl; and M is C₁₋₄ alkyl, hydrogen, or a cation which forms a substantially water-soluble salt with said compound at ambient temperatures.

3. A compound as claimed in claim 1 or claim 2, characterised in that a is 0, 1 or 2, and b is 0, 1 or 2.
4. A compound as claimed in claim 3, characterised in that a and b are independently 0, 1, or 2; wherein R is hydrogen or methyl; and wherein M is hydrogen, ammonium or alkali metal.
5. A compound as claimed in any preceding claim, characterised in that it has substantial water solubility.
6. A compound as claimed in claim 1, characterised in that it is N-vinyloxycarbonyl aspartic acid, N-vinyloxycarbonyl glutamic acid, N-vinyloxycarbonylglycine, N-vinyloxycarbonylalanine, N-vinyloxycarbonylaminobutyric acid, N-vinyloxycarbonylcysteine, N-vinyloxycarbonylornithine, N-vinyloxycarbonyliminodiacetic acid, or a salt thereof.
7. A polymeric compound comprising units of the formula V:



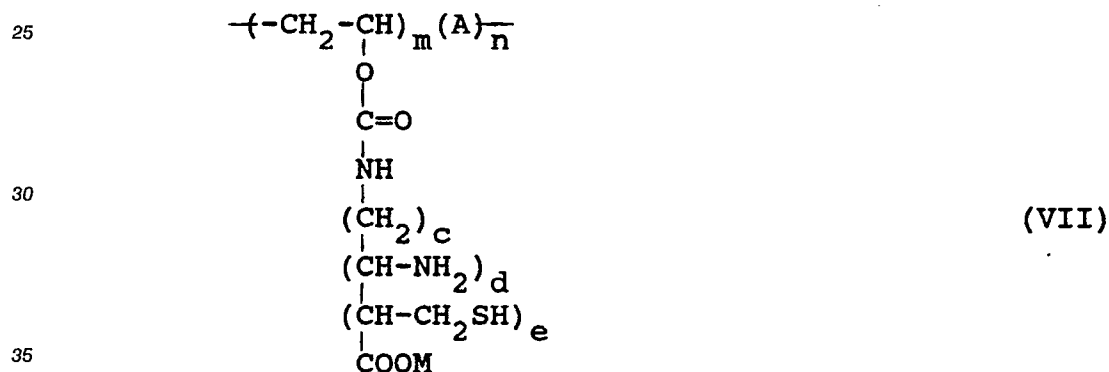
wherein m is an integer of at least 1; n is 0 or an integer of at least 1; M and X are as defined in claim 1; and A is a unit of at least one copolymerisable comonomer.

8. A polymeric compound as claimed in claim 7, characterised in that a is 0, 1 or 2 and b is 0, 1 or 2.
9. A polymeric compound as claimed in claim 7 or claim 8, characterised in that it comprises units of the formula VI:



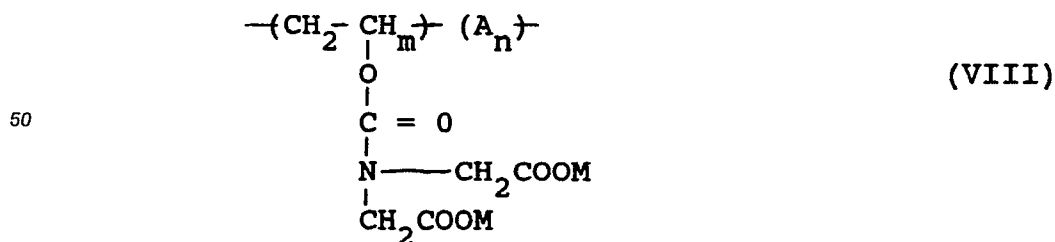
wherein m, n, A, a, b and M have the meanings given in claim 7.

10. A polymeric compound as claimed in claim 9 characterised in that a and b are independently 0, 1 or 2; wherein R is hydrogen or methyl and wherein M is hydrogen, ammonium or alkali-metal.
11. A polymeric compound as claimed in claim 9, characterised in that it comprises units of N-vinyloxycarbonyl aspartic acid or N-vinyloxycarbonyl glutamic acid.
12. A polymeric compound as claimed in claim 7 or claim 8, characterised in that it comprises units of the formula VII:



wherein m, n, A, c, d and e have the meanings given in claim 7.

13. A polymeric compound as claimed in claim 12, characterised in that it comprises units of N-vinyloxycarbonyl glycine, N-vinyloxycarbonyl alanine, N-vinyloxycarbonyl aminobutyric acid, N-vinyloxycarbonyl cysteine or N-vinyloxycarbonyl ornithine.
14. A polymeric compound, characterised in that it comprises units of the formula VIII:



wherein m, n, A and M have the meanings given in claim 7.

15. A polymeric compound as claimed in any one of claims 7 to 14, characterised in that the comonomer

providing the unit A is an ethylenically unsaturated monomer copolymerisable with vinyl acetate and/or ethylene.

- 5 **16.** A polymeric compound as claimed in any one of claims 7 to 15, characterised in that the comonomer is selected from unsaturated carboxylic acids and their salts, esters and derivatives; unsaturated dicarboxylic acids and their salts, esters, anhydrides and derivatives; unsaturated alcohols; unsaturated amines; unsaturated pyrroles; vinyl ethers; alkyl acrylates; alkenyl carboxyalkyl ethers; vinyl esters of carboxylic acids; alkenyl aryls; alkenyl aldehydes; acrylonitrile; methacrylonitrile; olefins and furans.
- 10 **17.** A polymeric compound as claimed in claim 16, characterised in that the comonomer is selected from acrylic acid, methacrylic acid, methyl methacrylate, crotonic acid, N-methylacrylyl-D- glucosamine, vinyl benzoic acid, vinyl acetic acid, methyl acrylate, itaconic acid, acrylamide, methyl acrylamide, fumaric acid, maleic acid, maleic anhydride, allyl alcohol, allyl amine, N-vinylpyrrolidinone, vinyl acetate, methyl methacrylate, methyl vinyl ether, vinyl benzene, vinyl pyridine, 4-hydroxy-2,6-pyridine
- 15 dicarboxylic acid, 2,6-pyridine dicarboxylic acid, acrolein, acrylonitrile, and methacrylonitrile.
- 18.** A polymeric compound as claimed in any one of claims 7 to 17, characterised in that the vinyl carbamate content is from 5 to 100%.
- 20 **19.** A polymeric compound as claimed in any one of claims 7 to 18, characterised in that it has substantial water solubility and a molecular weight of from 1000 to 750000.
- 20.** A polymeric compound as claimed in any one of claims 7 to 19, characterised in that it has a log K_{ca} of greater than 4.
- 25 **21.** A detergent composition characterised in that it comprises from 0.5% to 98% of a surfactant, and from 2% to 99.5% of a polymeric compound as claimed in any one of claims 7 to 20.

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